



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Selective organic matter preservation in "burn-down" turbidites on the Madeira Abyssal Plain

Citation for published version:

Prahl, FG, Cowie, GL, De Lange, GJ & Sparrow, MA 2003, 'Selective organic matter preservation in "burn-down" turbidites on the Madeira Abyssal Plain', *Paleoceanography*, vol. 18, no. 2, pp. 1-13.
<https://doi.org/10.1029/2002PA000853>

Digital Object Identifier (DOI):

[10.1029/2002PA000853](https://doi.org/10.1029/2002PA000853)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

Paleoceanography

Publisher Rights Statement:

Published in Paleoceanography by the American Geophysical Union (2003)

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Selective organic matter preservation in “burn-down” turbidites on the Madeira Abyssal Plain

F. G. Prahl,¹ G. L. Cowie,² G. J. De Lange,³ and M. A. Sparrow¹

Received 23 September 2002; revised 1 April 2003; accepted 17 April 2003; published 25 June 2003.

[1] Oxidized intervals of five organic-rich Madeira Abyssal Plain (MAP) turbidites deposited during the Miocene, Pliocene, and Pleistocene all displayed comparable major loss of total organic carbon (TOC) ($84 \pm 3.1\%$) accompanied by a negative isotopic ($\delta^{13}\text{C}$) shift ranging from -0.3 to -2.9% . Major but significantly lower loss of total nitrogen (N_{tot} , $61 \pm 7.1\%$) also occurred, leading to a decrease in TOC relative to N_{tot} ($\text{C}/\text{N}_{\text{tot}}$) and a $+1.3$ to 2.7% N_{tot} isotopic ($\delta^{15}\text{N}$) shift. Compound specific isotopic measurements on plant wax n-alkanes indicate the terrestrial organic component in the unoxidized deposits is ^{13}C -enriched owing to significant C_4 contribution. Selective preservation of terrestrial relative to marine organic carbon could account for the $\delta^{13}\text{C}$ behavior of TOC upon oxidation but only if a ^{13}C -depleted component of the bulk terrestrial signal is selectively preserved in the process. Although the $\text{C}/\text{N}_{\text{tot}}$ decrease and positive $\delta^{15}\text{N}$ shift seems inconsistent with selective terrestrial organic preservation, results from analysis of a Modern eolian dust sample collected in the vicinity indicate these observations are compatible. Regardless of the specific explanation for these isotopic observations, however, our findings provide evidence that paleoreconstruction of properties such as pCO_2 using the $\delta^{13}\text{C}$ of TOC is a goal fraught with uncertainty whether or not the marine sedimentary record considered is “contaminated” with significant terrestrial input. Nonetheless, despite major and selective loss of both marine and terrestrial components as a consequence of postdepositional oxidation, intensive organic geochemical proxies such as the alkenone unsaturation index, U_{37}^{K} , appear resistant to change and thereby retain their paleoceanographic promise. **INDEX TERMS:** 1040 Geochemistry: Isotopic composition/chemistry; 1055 Geochemistry: Organic geochemistry; 1030 Geochemistry: Geochemical cycles (0330); 3022 Marine Geology and Geophysics: Marine sediments—processes and transport; 4267 Oceanography: General: Paleooceanography; **KEYWORDS:** turbidites, diagenesis, organic carbon, stable carbon isotopes, lipid biomarkers

Citation: Prahl, F. G., G. L. Cowie, G. J. De Lange, and M. A. Sparrow, Selective organic matter preservation in “burn-down” turbidites on the Madeira Abyssal Plain, *Paleoceanography*, 18(2), 1052, doi:10.1029/2002PA000853, 2003.

1. Introduction

[2] The discovery of massive distal turbidites on the Madeira Abyssal Plain (MAP) has proven invaluable for advancing fundamental understanding of various issues related to redox geochemistry [Weaver *et al.*, 1998, and references therein]. This value is particularly apparent to those in the organic geochemistry community investigating controls on organic matter preservation in marine sediments [Hartnett *et al.*, 1998, and references therein]. Examination of diffusion-limited, aerobic oxidation phenomenon operating on the upper portion of organic-rich MAP turbidite deposits [Thomson *et al.*, 1987; Wilson *et al.*, 1985; Buckley and Cranston, 1988] reveals that dissolved oxygen availability plays an undeniable, primary role in organic matter preservation [de Lange *et al.*, 1994; Keil *et al.*, 1994; Cowie

et al., 1995]. However, the specific source of organic carbon residual in the deposit as a consequence of this aerobic oxidation phenomenon, often referred to as a “burn-down” event, is yet to be illuminated unequivocally. Some argue that residual organic carbon is predominantly a marine component in the original turbidite that resists aerobic oxidation and, as a consequence of the “burn-down” event, is selectively preserved relative to total organic carbon (TOC) [Cowie *et al.*, 1998; Hoefs *et al.*, 1998a]. However, others contend selective preservation of a terrestrial organic carbon component, clearly present at some level in the original turbidite, accounts for much of the compositional character of the residual TOC [Prahl *et al.*, 1997]. Clear resolution of these contrasting viewpoints is a challenge since much of the TOC in the turbidites, and in particular, its “burn-down” intervals, is uncharacterizable on a detailed molecular basis [Cowie *et al.*, 1995].

[3] Both alternatives have specific merits that lend them credibility. For this reason, we investigated in the present study further organic geochemical details of the “burn-down” phenomenon in discrete sets of MAP samples taken from well-above and well-below the aerobic oxidation front identified in Pliocene and Miocene-age turbidites collected on ODP Leg 157 [Weaver *et al.*, 1998] and in a more stratigraphically resolved set of samples taken across this

¹College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, Oregon, USA.

²Marine Geosciences Unit, Geology and Geophysics Department, University of Edinburgh, Edinburgh, UK.

³Institute of Earth Sciences, Department of Geochemistry, Utrecht University, Utrecht, Netherlands.

boundary identified in the Pleistocene-age f-turbidite already studied quite extensively by others [Prah et al., 1989, 1997; de Lange, 1992, 1995; de Lange et al., 1994; Keil et al., 1994; Cowie et al., 1995]. Specific analytical targets were trace-level organic geochemical properties including: plant wax n-alkane (ΣC_{25-31}) and long chain alkenone (LCK) concentrations and composition, plus compound-specific carbon isotopic measurements of both; and concentrations for a variety of biomarkers which were dominant gas chromatographically resolved components of the “free” and “bound” lipid extracts of these deposits. The objective of our effort was threefold: (1) to put our new lipid biomarker data and that recently published by others [Hoefs et al., 2002] into clear perspective with the now well-documented description for bulk properties (i.e., calcium carbonate, total organic carbon and nitrogen plus stable isotopic composition of both) in a wide collection of these organic-rich MAP deposits [Cowie et al., 1998; de Lange, 1998], (2) to seek further evidence for selective preservation/degradation of organic matter [Hedges et al., 1999] in the aerobic “burn-down” intervals of these turbidites and, in particular, (3) to determine more confidently whether such selectivity results in preferential enrichment in the oxidized deposits of a significant [Prah et al., 1997] and not just a trace level [Hoefs et al., 2002] terrestrial organic carbon signal.

2. Experiment

2.1. Sample Collection

[4] Three piston cores were collected from MAP by the Dutch Geological Survey (RDG) in 1986 (86P5: 32° 2.5'N 24° 12.5'W; 86P25: 30° 44.2'N 25° 22.5'W) and on a cruise organized by the Dutch Science Foundation (NWO) in 1990 (90P22: 32° 3.0'N 24° 12.1'W). A set of samples representing oxidized and unoxidized intervals of the Pleistocene age f-turbidite identified in each of these cores was obtained as soon as possible after collection [Prah et al., 1997]. Immediately upon sampling, each ~10 cm thick, wet sediment interval was stored frozen in a clean glass jar until needed for detailed organic geochemical analysis.

[5] Two drill cores (Holes 951A and 951B) were also recovered from MAP during Leg 157 of the Ocean Drilling Program (ODP) [Weaver et al., 1998]. Intervals of ~10 cm thickness were sampled from depth horizons spanning four oxidation fronts (two in each core) of Pliocene to Miocene age [de Lange, 1998]. Each was freeze-dried and stored in a clean glass jar until needed for detail organic geochemical analysis.

[6] A single eolian dust sample collected near the Canary Islands was also obtained for analysis. This dust sample was one of a large archive (Roy Chester, University of Liverpool), a subset of which was analyzed recently for plant wax isotopic composition [Huang et al., 2000].

2.2. Analytical Measurements

[7] Total organic carbon (TOC) content and its stable isotopic composition ($\delta^{13}C$), total nitrogen (N_{tot}) content and its stable isotopic composition ($\delta^{15}N$), and inorganic carbon (as $CaCO_3$) content in freeze-dried subsamples of

each interval were analyzed in prior studies [Cowie et al., 1998; de Lange, 1998; de Lange et al., 1994; Prah et al., 1997]. Data for these bulk properties reported herein have been previously published but are collated by us to facilitate discussion of our new lipid biomarker results. The same bulk properties of the dust sample were also measured in our study using common analytical methods.

2.3. Lipid Biomarker Isolation and Quantification

[8] Total solvent extractable lipids (TEL or “free” lipids) were released from either wet or freeze-dried samples (~3–5 g dry) by standard sohxlet or ultrasonic extraction methods. The solvent mixture of toluene or methylene chloride in methanol employed for extraction (~60 mL total) and containing TEL was then partitioned using a separatory funnel into hexane (20 mL, 3 times) after addition of water (~15 mL). The combined hexane layers were dried over anhydrous Na_2SO_4 and rotary evaporated to just dryness. The resultant TEL residue was subsequently separated by silica gel column chromatography into compound classes (n-alkanes, methyl/ethyl ketones, n-alkyl ketols/diols) for quantitative analysis by capillary gas chromatography with flame ionization detection (GC-FID). Prior to GC-FID analysis, the fraction containing n-alkyl ketols/diols was derivatized using N,O-bis-trifluorotrimethylacetamide with 1% trichloromethylsilane (BSTFA, Sigma). Further details of the procedure for isolation and GC-FID analysis of specific compounds in the “free” lipid extracts are given elsewhere [Prah et al., 1997].

[9] “Bound” lipids were then isolated from a subset of samples from core 90P22 that had previously been extracted for “free” lipids. Release of “bound” lipids was accomplished by suspension of the pre-extracted sediment in methanol (~60 mL), addition of sufficient concentrated HCl to dissolve $CaCO_3$ in the sample and yield a pH of ~1, and boiling of this mixture under reflux (~2–3 hours). Upon removal of solids by centrifugation, the acidic, methanolic solution was then partitioned into hexane, which was subsequently handled as described above for “free” lipid extracts. The resultant total “bound” lipid residue was sequentially derivatized first using 14% BF_3 in methanol (Pierce Biotechnology) and then BSTFA before GC-FID analysis.

[10] Quantification of all compounds targeted by GC-FID was accomplished using an internal standard method. Prior to extraction of “free” and “bound” lipids, appropriate standards were spiked into the sediment to act as internal yield tracers for recovery correction (ISTD). ISTDs used were: 3-methyltricosane for n-alkanes, nonadecan-2-one for methyl/ethyl ketones, 5 α androstanol for n-alkyl ketols/diols and 2-methylheneicosanoic acid for “bound” lipids. ISTD recovery through the entire procedure was typically 70–80% or better. All reported quantitative results for individual “free” and “bound” lipid biomarkers have been corrected using recovery data for the corresponding standard.

[11] The identity of all quantified compounds was determined by interpretation of mass spectra obtained using a benchtop HP5971A GC mass spectrometer. Representative electron impact mass spectra for the reported $C_{30:1}$ and C_{30}

ketols and C₃₀ diol are described by *de Leeuw et al.* [1981] and *Versteegh et al.* [1997].

2.4. Compound-Specific Isotope Analyses

[12] In selected cases, n-alkane and methyl/ethyl ketone fractions isolated from samples were purified in preparation for compound-specific carbon isotope analysis (irmGCMS) [Hayes et al., 1990]. Urea adduction was used as the purification step for n-alkane fractions [Prahl et al., 1992]. This treatment separated the C_{25,27,29} and C₃₁ n-alkanes targeted for analysis from potential coeluting apolar compounds and/or the unresolved complex mixture (UCM). Saponification by refluxing with ethanolic-KOH [Christie, 1973] was used as the purification step for methyl/ethyl ketone fractions. This treatment separated the diunsaturated C₃₇ methyl ketone (K37:2) targeted for irmGCMS analysis from an interfering, source-related diunsaturated C₃₆ methyl ester.

[13] irmGCMS measurement of carbon isotopic composition ($\delta^{13}\text{C}$, in ‰ versus PDB) for each analytical target in the purified fractions was accomplished using an HP5890A gas chromatograph equipped with a capillary column (DB-1, 60 m \times 0.32 mm i.d., 0.5 μm film thickness) and interfaced [Hayes et al., 1990] to a Finnigan Delta S mass spectrometer. Replicate sample analyses indicated the precision of reported $\delta^{13}\text{C}$ measurements on individual compounds was typically $\pm 0.5\text{‰}$. Co-injection of standards of known isotopic composition (perdeuterated nC₃₆, -27.09‰ and nondeuterated nC₄₀, -32.15‰) indicated the accuracy of their determinations was within a comparable tolerance.

3. Results

3.1. Intracomparison of Unoxidized Turbidite Intervals

[14] All unoxidized turbidite intervals examined in this study were organic matter-rich, containing from 0.9 to 1.7% total organic carbon (TOC) by weight (Table 1). The deposits of early Pliocene-age showed highest TOC. Calcium carbonate content varied widely, ranging from 8.5 to $\sim 50\%$ by weight with highest values evident in the Pleistocene-age deposits.

[15] Elemental composition gauged by the molar ratio of TOC to total nitrogen (C/N_{tot}) was relatively invariant in the unoxidized turbidites, ranging from 10.5 to 13.2 and averaging 11.8 ± 1.0 (n = 14). Such compositional uniformity was also apparent in isotopic data for TOC ($\delta^{13}\text{C}$) and total nitrogen ($\delta^{15}\text{N}$) which both showed only $\sim 1\text{‰}$ variation in the complete data set. Carbon and nitrogen isotopic values ranged from -19.3 to -20.3‰ and from 4.0 to 4.9‰, respectively.

[16] Significantly more compositional heterogeneity was apparent in the data set for lipid biomarkers of terrestrial (C_{25,27,29,31} plant wax n-alkanes $\equiv \Sigma\text{C}_{25-31}$) and marine (C₃₇₋₃₉ alkenones $\equiv \text{LCK}$) origin. TOC-normalized concentrations for each displayed an equally large, three-fold variation. These properties directly correlate (r = +0.82) with highest concentration for each evident in the Pleistocene-age deposits. Alkenone unsaturation patterns (U_{37}^K) also varied widely from ~ 0.7 in the Pleistocene-age deposits to ≥ 0.9 in the older deposits, suggesting very different

thermal conditions in surface waters at the time marine organic matter in each turbidite was initially deposited on the continental slope off NW Africa [de Lange et al., 1987]. Based on an established calibration ($U_{37}^K = 0.034T + 0.039$) [Prahl et al., 1988], a difference in surface water temperature of $\sim 7^\circ\text{C}$ is inferred from the U_{37}^K measurements. Despite surface water temperatures spanning an apparent absolute range from ~ 20 to 27°C , $\delta^{13}\text{C}$ composition of the dominant phytoplankton-derived alkenone, K37:2 [Brassell, 1993], differed by only 1‰ between the deposits (Table 2). Notably, this small range of isotopic variation for this biomarker matches that observed for TOC.

[17] $\delta^{13}\text{C}$ values for individual n-alkanes of purported terrestrial plant wax origin [Prahl et al., 1997] measured in the Pleistocene-age deposit were not identical. Results from analysis of the same turbidite sampled at two different geographic sites, more than 100 km apart, show the isotopic composition of nC₂₉ was consistently $\sim 2\text{‰}$ more ^{13}C -depleted than either nC₂₇ or nC₃₁ and $\sim 1\text{‰}$ more ^{13}C -enriched than plant wax n-alkanes identified in a Modern eolian dust sample in the vicinity of the nearby Canary Islands (Table 2). Eolian dust showed little variability in its δ values for nC_{27,29} and C₃₁ (Table 2) and could otherwise, based on similarity of its gas chromatographic fingerprint, represent a clear source of such terrestrial biomarkers in these turbidite deposits [Prahl et al., 1997].

3.2. Intracomparison of Oxidized With Unoxidized Turbidite Intervals

[18] Results also show the aerobic “burn-down” event [Thomson et al., 1987; Wilson et al., 1985; Buckley and Cranston, 1988] caused common compositional changes in all organic-rich MAP turbidites analyzed (Table 1). Loss of TOC was major, averaging $84 \pm 3.1\%$, and relatively constant on an absolute scale ($\sim 9.1 \times 10^{-4}$ $\mu\text{mol TOC/g}$, $\pm 24\%$ 1 σ). TOC loss is accompanied by a much more variable absolute loss of inorganic carbon (13×10^{-4} $\mu\text{mol C/g}$, $\pm 64\%$ 1 σ). Dissolution of calcium carbonate by acidity generated from aerobic decomposition of organic matter and oxidation of reduced sulfur during the “burn-down” event [de Lange, 1998] is the probable cause of the inorganic carbon loss. TOC loss was also accompanied by a negative shift in the $\delta^{13}\text{C}$ composition of the residual organic material. Although the shift was consistently negative, averaging -1.7‰ , its magnitude was not the same in each deposit, varying from -0.3 to -2.9‰ .

[19] Loss of total nitrogen (N_{tot}) from the deposits was major, averaging $61 \pm 7.1\%$, but notably less than that for TOC. Preferential loss of TOC relative to N_{tot} led to a decrease in C/N_{tot}. C/N_{tot} measured in oxidized intervals ranged from 3.2 to 5.6, averaging 4.7 ± 0.9 . Lowest values in the range were below what can be explained by common forms of organic matter, implying significant inorganic contribution to N_{tot} in the oxidized deposit [de Lange, 1992, 1998; Cowie et al., 1998]. Depending on the turbidite considered, loss of N_{tot} resulted in a significant positive shift in $\delta^{15}\text{N}$ for residual total nitrogen of +1.3 to +2.7‰, averaging +1.8‰.

[20] Major fractions of the lipid biomarkers attributable to both terrestrial (ΣC_{25-31}) and marine (LCK) carbon sources

Table 1. Summary of Organic Geochemical Measurements in Oxidized (ox) and Unoxidized (unox) Intervals of Various MAP Turbidities

| Core Code | Depth, cm | Emplacement Age | Status | CaCO ₃ , wt % | Percent Loss ^a | TOC, wt % | Percent Loss ^a | C/N, mol | N _{tot} , Percent Loss ^a | δ ¹³ C, ‰ | δ ¹⁵ N, ‰ | ΣC _{25–31} , μg/gC | Percent Loss ^a | LCK, μg/gC | Percent Loss ^a | U ₃₇ ^{K'} |
|----------------------------------|-----------|------------------|--------|--------------------------|---------------------------|-----------|---------------------------|----------|--|----------------------|----------------------|-----------------------------|---------------------------|------------|---------------------------|-------------------------------|
| Eolian Dust ^b 86P5 | 704–714 | Modern 140 ky | ox | 6.8 | 0.93 | | | 10.0 | | –16.7 | 10.9 | 320 | | | | |
| | 751–761 | | unox | 48.5 | 12 | 0.16 | | 4.5 | 61 | –23.0 | ~6–6.5 | 380 | 47 | 590 | 91 | 0.716 |
| | 772–782 | | unox | 51.7 | | 0.93 | | 10.6 | | –20.2 | ~5 | 120 | | 1100 | | 0.705 |
| 86P25 | | | | 51.8 | | 0.94 | | 11.2 | | –20.1 | ~5 | 110 | | 960 | | 0.685 |
| | 780–789 | 140 ky | ox | 47.9 | 10 | 0.21 | | 5.3 | 60 | –21.9 | ~6–6.5 | 280 | 34 | 590 | 86 | 0.716 |
| | 855–868 | | unox | 50.7 | | 1.0 | | 10.6 | | –20.2 | ~5 | 88 | | 860 | | 0.712 |
| 951A/15X/3 | 905–906 | | unox | 50.5 | | 1.0 | | 11.1 | | –20.2 | ~5 | 79 | | 860 | | 0.699 |
| | 7–15 | Late Pliocene | ox | 0.4 | 96 | 0.26 | | 5.6 | 57 | –19.6 | 5.9 | 110 | 47 | 124 | 95 | 0.918 |
| | 46–54 | | unox | 8.5 | | 1.3 | | 13.1 | | –19.3 | 4.5 | 36 | | 421 | | 0.912 |
| 951A/19X/2 | 69–76 | | unox | 8.9 | | 1.3 | | 13.2 | | –19.3 | 4.4 | 39 | | 444 | | 0.907 |
| | 4–9 | Early Pliocene | ox | 23.4 | 47 | 0.23 | | 5.2 | 68 | –21.2 | 7.2 | 143 | 52 | 76 | 98 | 0.923 |
| | 22–32 | | unox | 36.6 | | 1.5 | | 12.6 | | –19.9 | 4.4 | 38 | | 589 | | 0.911 |
| 952A/15H/1 | 44–53 | | unox | 36.7 | | 1.5 | | 12.7 | | –19.8 | 4.7 | 41 | | 696 | | 0.913 |
| | 63–72 | | unox | 36.7 | | 1.4 | | 12.8 | | –19.7 | 4.7 | 37 | | 593 | | 0.910 |
| | 7–14 | early Pliocene | ox | 5.1 | 88 | 0.25 | | 4.4 | 68 | –20.9 | 7.0 | 147 | 61 | 134 | 98 | 0.915 |
| 952A/15H/2 | 64–72 | | unox | 29.1 | | 1.7 | | 12.8 | | –19.5 | 4.7 | 38 | | 615 | | 0.889 |
| | 59–67 | | unox | 32.0 | | 1.6 | | 12.1 | | –19.4 | 4.2 | 48 | | 672 | | 0.894 |
| 952A/15H/3 | 18–26 | | unox | 30.2 | | 1.6 | | 12.1 | | –19.5 | 4.0 | 41 | | 623 | | 0.899 |
| | 44–50 | late Miocene | ox | 0.8 | 96 | 0.25 | | 3.2 | 50 | –22.3 | 6.7 | 115 | 57 | 49 | 99 | 0.956 |
| | 61–71 | | unox | 15.9 | | 1.4 | | 10.5 | | –19.9 | 4.9 | 40 | | 716 | | 0.946 |
| 952A/27X/4 | 82–92 | | unox | 16.0 | | 1.4 | | 10.7 | | –19.8 | 4.9 | 41 | | 576 | | 0.949 |

^aPercent loss defined by $1 - [\text{ox}]/[\text{unox}] \times 100$, where [ox] and [unox] are the calcium carbonate-free, dry weight concentration measured in the oxidized and unoxidized turbidite interval, respectively.^bEolian dust sample collected near the Canary Islands by Roy Chester; see text for details.

Table 2. $\delta^{13}\text{C}$ of TOC, Specific Plant Wax n-Alkanes (nC_{25} , nC_{27} , nC_{29} , nC_{31}) and the Diunsaturated Alkenone K37:2 in an Eolian Dust and Various Unoxidized (Unox) MAP Turbidite Samples^a

| Core Code | Depth, cm | Emplacement Age | Status | TOC, ‰ | nC_{25} , ‰ | nC_{27} , ‰ | nC_{29} , ‰ | nC_{31} , ‰ | K37:2, ‰ |
|-------------|-----------|-----------------|--------|--------|----------------------|----------------------|----------------------|----------------------|----------|
| Eolian Dust | | Modern | | -16.7 | -25.4 | -27.8 | -27.8 | -26.3 | NA |
| 86P25 | 855–868 | 140 kyr | unox | -20.2 | -27.0 | -23.9 | -26.1 | -23.9 | ND |
| 90P22 | 75–76 | 140 kyr | unox | -20.3 | -24.7 | -24.1 | -26.4 | -24.8 | -22.8 |
| 90P22 | 82–83 | 140 kyr | unox | -20.3 | ND | ND | ND | ND | -22.8 |
| 951A/15X/3 | 46–54 | Late Pliocene | unox | -19.3 | ND | ND | ND | ND | -22.0 |
| 951A/19X/2 | 22–32 | Early Pliocene | unox | -19.9 | ND | ND | ND | ND | -23.0 |
| 952A/15H/2 | 59–67 | Early Pliocene | unox | -19.4 | ND | ND | ND | ND | -22.3 |
| 952A/27X/4 | 61–71 | Late Miocene | unox | -19.9 | ND | ND | ND | ND | -22.1 |

^aAbbreviations are as follows: NA, not applicable; ND, not determined.

were also lost from all deposits by the “burn-down” event. As previously documented for the Pleistocene age f-turbidite [Prah *et al.*, 1997], loss in every case was greater for LCK ($94 \pm 4.9\%$) than ΣC_{25-31} ($49 \pm 9.4\%$). Furthermore, LCK displayed consistently greater reactivity than TOC while ΣC_{25-31} displayed less (Figure 1). The consequence of this selectivity during the “burn-down” event is that TOC-normalized concentrations for LCK decreased while those for ΣC_{25-31} increased. Despite major absolute quantitative loss of LCK, the U_{37}^{K} signature of this biomarker series showed relative insensitivity to alteration, changing by ≤ 0.02 units.

3.3. Stratigraphic Trends in the Oxidized Turbidite Interval

[21] Nine samples collected stratigraphically just above the oxidation front identified in core 90P22 were analyzed for TOC content and $\delta^{13}\text{C}$ composition (Table 3). In addition, “free” lipid extracts from each were analyzed for four compounds of phytoplankton origin (LCK, C30:1 and C30 ketols, C30 diol) as well as for two homologous n-alkyl series of terrestrial origin (ΣC_{25-31} and even carbon n-alcohols $\equiv \Sigma\text{FAlc}_{20-32}$). “Bound” lipid fractions released by acid-hydrolysis of the sediment after “free” lipids had been extracted were also analyzed quantitatively for nC_{16} , $\text{nC}_{16:1}$, nC_{18} and nC_{24} fatty acids (FA) and nC_{24} fatty alcohol (FAlc). This set of individual “free” and “bound” compounds represent the dominant, gas chromatographically (GC)-resolved lipid biomarker features detected in these deposits.

[22] The specific phytoplanktonic source(s) of the C30:1 and C30 ketol and the C30 diol is unknown [Versteegh *et al.*, 1997]. “Bound” C24 FA and FAlc are the major constituents of even-carbon predominant homologous series of each compound class (Figure 2). Of these compound classes, the fatty acid series is the most abundant, GC-resolved component of the total “bound” lipid extracts. Presence of such “bound,” long-chain ($>\text{C}_{20}$) n-alkyl series provides further evidence that terrestrial sources [Kolattukudy, 1976] contribute organic carbon to these deposits at some quantitative level. Notably, the “burn-down” event caused a shift in the carbon maximum for the FA series from nC_{26} in the unoxidized turbidite to nC_{24} in the oxidized interval (compare top with bottom of left-hand panel in Figure 2). Such a conspicuous change due to the oxidation phenomena was not apparent in the compositional characteristics of homologous series for “bound” FAlc (compare top with bottom right-hand panel in Figure 2) or

other “free” n-alkyl lipids of purported terrestrial origin in these deposits [Prah *et al.*, 1997].

[23] Table 3 summarizes the quantitative behavior of the various “free” and “bound” lipid biomarkers analyzed in core 90P22 to the “burn-down” event. Full impact of the oxidation on any of the measured properties was not evident until several centimeters above the sharp color transition [de Lange, 1998] separating the oxidized from the unoxidized portion of the deposit. Upon reaching full impact, all “free” phytoplankton biomarkers and $\Sigma\text{FAlc}_{20-32}$ display a similar percentage degradation and, as described above, a significantly greater percentage loss than TOC. On the other hand,

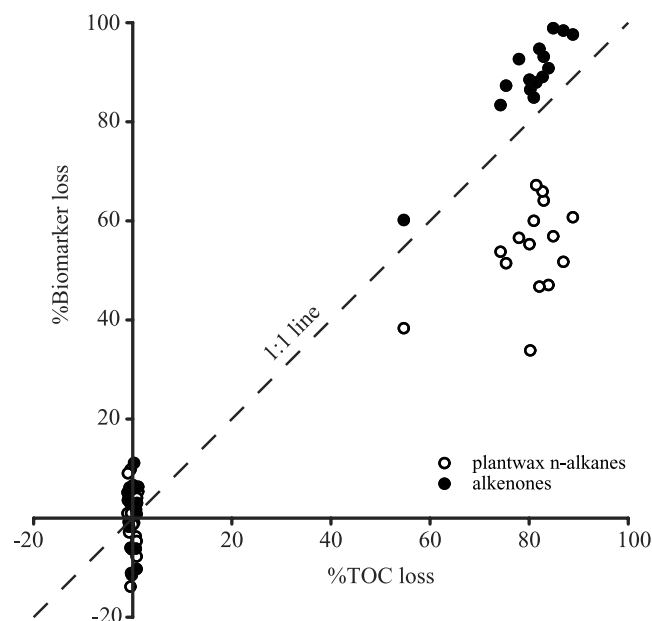


Figure 1. Scatterplot showing quantitative relationship between the percentage loss of two different types of lipid biomarkers and total organic carbon (TOC) from the various turbidites examined in this study as a consequence of the aerobic “burn-down” phenomenon (all data from Tables 1 and 3). Plant wax n-alkanes represent a terrestrial component of organic carbon while alkenones represent a marine phytoplankton component. Scatter in data plotted at the origin reflects inhomogeneity in the biomarker and TOC composition of the unoxidized turbidite. The dashed line demarks the projection for one-to-one loss of biomarker and TOC.

Table 3. Stratigraphic Record for Percent Loss of Various Free and Bound Lipid Biomarkers in Oxidized Intervals of the MAP f-Turbidite (90P22 #2)

| Depth, cm ^a | TOC, Percent Loss ^b | $\delta^{13}\text{C}$ Shift ^c | Phytoplankton Biomarkers | | | | Terrestrial Plant Waxes | | | | Bound Lipids | | | | | | | |
|----------------------------|--------------------------------------|---|--------------------------|---|---|--|---|---|--|--|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|--|-----------------|-----------------|-----------------|
| | | | LCK, Percent Loss | U_{37}^K , Shift ^b | $\text{C}_{30:1}$ Ketol, Percent Loss | C_{30} Diol, Percent Loss | C_{30} Ketol, Percent Loss | ΣC_{25-31} , Percent Loss | $\Sigma\text{FALC}_{22-30}$ Percent Loss | C16:1 FA , Percent Loss | C16 FA , Percent Loss | C18 FA , Percent Loss | C24 FA , Percent Loss | C24 FA , Percent Loss | C24 Falc , Percent Loss | | | |
| | | | | | | | | | | | | | | | | | | |
| Oxidized | | | | | | | | | | | | | | | | | | |
| 39.5 (1062.5) | 78 | -2.2 | 93 | 0.051 | 95 | 97 | 97 | 47 | 87 | | | | | | | | | |
| 40.5 (1063.5) | 83 | -1.9 | 93 | 0.055 | 94 | 94 | 93 | 51 | 86 | | | | | | | | | |
| 46.0 (1069.0) | 83 | -2.4 | 89 | -0.016 | 94 | 95 | 93 | 47 | 87 | | | | | | | | | |
| 52.5 (1075.5) | 75 | -2.6 | 87 | -0.016 | 92 | 94 | 95 | 52 | 87 | | | | | | | | | |
| 53.5 (1076.5) | 80 | -1.7 | 89 | 0.020 | 90 | 93 | 92 | 44 | 85 | | | | | | | | | |
| 56.5 (1079.5) | 81 | -1.6 | 88 | 0.041 | 90 | 92 | 91 | 50 | 84 | | | | | | | | | |
| 61.5 (1084.5) | 81 | -2.2 | 85 | -0.018 | 91 | 93 | 91 | 46 | 86 | | | | | | | | | |
| 65.5 (1088.5) | 74 | -0.9 | 83 | 0.020 | 86 | 90 | 86 | 38 | 78 | | | | | | | | | |
| 71.0 (1094.0) | 55 | -0.6 | 60 | -0.027 | 77 | 79 | 75 | 35 | 71 | -10 | -2 | -3 | 50 | 22 | | | | |
| cm | Weight Percent | % | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ | $\mu\text{g/g}$ |
| Unoxidized ^d | | | | | | | | | | | | | | | | | | |
| 75.5 (1098.5) | 1.8 | -20.3 | 35 | 0.686 | 1.2 | 1.4 | 1.3 | 2.1 | 3.1 | 0.52 | 2.9 | 1.3 | 0.94 | 0.24 | | | | |
| 82.5 (1105.5) | 1.8 | -20.3 | 30 | 0.673 | 1.5 | 1.5 | 1.3 | 2.0 | 2.9 | 0.73 | 3.6 | 1.7 | 0.98 | 0.27 | | | | |
| 94.5 (1117.5) | 1.8 | -20.2 | 31 | 0.669 | 1.3 | 1.0 | 1.0 | 1.8 | 2.8 | 0.57 | 3.6 | 1.7 | 0.88 | 0.22 | | | | |
| Average | 1.8 | -20.3 | 32 | 0.676 | 1.3 | 1.3 | 1.2 | 2.0 | 2.9 | 0.61 | 3.3 | 1.6 | 0.93 | 0.24 | | | | |
| Standard Deviation | 0.02 | 0.1 | 2.9 | 0.009 | 0.11 | 0.24 | 0.18 | 0.18 | 0.14 | 0.11 | 0.38 | 0.24 | 0.050 | 0.027 | | | | |
| Percent Standard Deviation | 0.88 | | 9 | 1.3 | 8 | 18 | 15 | 9 | 5 | 18 | 11 | 15 | 5 | 11 | | | | |

^aDepth in section 2 (depth in core 90P22).^bPercentage loss; see Table 1 for definition.^cDifference in the stable carbon isotopic composition of TOC (or U_{37}^K of alkenones $\equiv \text{LCK}$) in oxidized relative to average unoxidized turbidite interval.^dAll concentrations are normalized to calcium carbonate-free sediment weight.

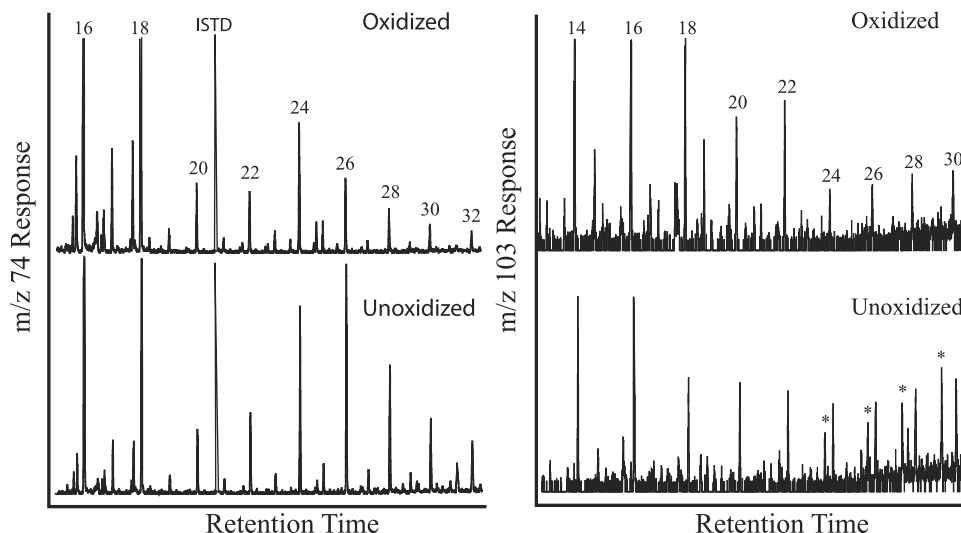


Figure 2. Comparison of mass fragmentograms for homologous series of bound n-fatty acids (as methyl esters, m/e 74) and alcohols (as trimethyl silyl ethers, m/e 103) released from oxidized (top panels) and unoxidized (bottom panels) intervals of the MAP f-turbidite identified in core 90P22. Numbers indicate the carbon chain length for corresponding peaks in the respective top and bottom chromatograms. Asterisks identify a series of $C_{24,26,28,30}$ β -hydroxy n-fatty acids only significantly detected in the unoxidized intervals. ISTD identifies the aiC21 fatty acid added to each sample for purposes of recovery correction.

the “bound” long-chain, even carbon dominant, fatty acid and alcohol series of purported terrestrial origin and depicted quantitatively by data for C_{24} FA and FAlc in Table 3 display, like ΣC_{25-31} , lower percentage degradation than TOC. The $C_{16:1}$, C_{16} and C_{18} fatty acids, common constituents of microbial membranes [Goossens *et al.*, 1986], display negative percentage loss or an increase in absolute amount, a feature explainable by production within the deposit. On this basis, we speculate that some fraction of these compounds has been introduced by microflora, which actually mediate the aerobic “burn-down” phenomenon [Buckley and Cranston, 1988].

[24] In contrast to all other examinations of the “burn-down” event (Table 1) [Prahl *et al.*, 1989; Hoefs *et al.*, 1998b], the small differences noted in $U_{37}^{K'}$ between the oxidized and unoxidized intervals are not consistently positive and the stratigraphic trend for observed shifts in $U_{37}^{K'}$ follows no clear pattern. Despite major loss of LCK from the oxidized deposit, $U_{37}^{K'}$ again shows minimal impact.

4. Discussion

4.1. Isotopic Constraints on Organic Carbon Components

[25] The presence of plant wax lipids [Prahl *et al.*, 1997], lignin phenols [Cowie *et al.*, 1995] and grass pollen [Keil *et al.*, 1994] in the MAP deposits makes unequivocal the conclusion that terrestrial sources contribute at some level to the TOC content of the MAP f-turbidite deposit in both its unoxidized and oxidized form. Using a simple binary mixing model, Prahl *et al.* [1997] concluded that selective preservation of a ^{13}C -depleted, less reactive but not inert terrestrial component accounts for the negative isotopic shift

of residual organic carbon left behind by the aerobic “burn-down” phenomenon. End members for the isotopic composition of marine and terrestrial organic carbon sources required in the model were both assumed to be fixed values, insensitive to change throughout the entire “burn-down” event. In view of our new data, this assumption is objectively reconsidered in the following discussion.

4.2. Marine Organic Carbon

[26] The value used in the model for the marine isotopic end member ($\delta^{13}C_{mar}$) was obtained from a scatterplot for TOC-normalized plant wax n-alkane concentration versus $\delta^{13}C$ of TOC. Extrapolation of the equation for the linear least squares fit of the f-turbidite data to zero biomarker concentration yielded a value of -19.1‰ . Figure 3 shows such a scatterplot updated with the complete set of data now available for MAP “burn-down” turbidites of all ages (Tables 1 and 3). Data for each of the three geological periods of turbidite deposition (Pleistocene, Pliocene, Miocene) are distinguished on the graph and fitted individually by least squares analysis to a line. Virtually the same equation defines data sets for the Pleistocene and Pliocene age deposits, while that for the older Miocene age deposit differs quite markedly. One explanation for this difference is that the terrestrial end member for plant wax n-alkane concentration has a much lower value in the Miocene age deposits than in the younger deposits. Whatever the cause for this difference, however, extrapolation of all three lines to zero biomarker concentration yields a notable finding, a consistent value ($-18.6 \pm 0.1\text{‰}$) for the putative $\delta^{13}C_{mar}$. This finding, which differs little from our original assignment [Prahl *et al.*, 1997], would suggest that marine organic carbon in all of these

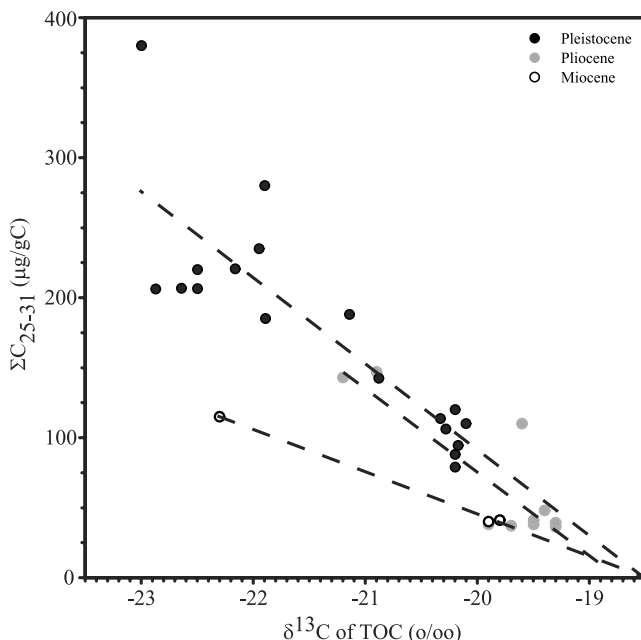


Figure 3. Scatterplot showing the relationship between TOC-normalized plant wax n-alkane (ΣC_{25-31}) concentration and $\delta^{13}C$ composition of TOC measured in all oxidized and unoxidized intervals of the Pleistocene, Pliocene and Miocene-age turbidites (all data from Tables 1 and 3). The dashed lines depict linear least squares fits of the data set for each turbidite age. Extrapolation of these lines to zero biomarker concentration yields an estimate of the average isotopic end member for the pure marine organic carbon component in these deposits ($\delta^{13}C_{\text{mar}} = -18.6 \pm 0.1\text{‰}$).

deposits has effectively the same average isotopic end member composition.

[27] We employed an independent approach to estimate $\delta^{13}C_{\text{mar}}$ and test the latter inference. Using irmGCMS, the $\delta^{13}C$ composition of K37:2, the dominant LCK in these deposits, was found to be quite uniform in the complete set of samples analyzed ($-22.4 \pm 0.4\text{‰}$, Table 2). Given that (1) carbon in the alkenones is $\sim 4.2\text{‰}$ ^{13}C -depleted relative to primary photosynthate of phytoplankton which biosynthesize these biomarkers [Popp *et al.*, 1998] and (2) this isotopic offset is relatively insensitive to variation in oceanographic factors which can influence cell physiology and biochemical synthesis, such as growth temperature and nutrient availability, $\delta^{13}C_{\text{mar}}$ can be assigned a value of -18.2‰ . This value matches quite well with that assigned above using the geochemical property-property scatterplot approach.

[28] Although encouraging, this agreement does not confirm the actual value for $\delta^{13}C_{\text{mar}}$, and may be fortuitous. Only a very small fraction of the organic carbon biosynthesized by phytoplankton and transported by sedimentary processes to the seafloor is preserved [Suess, 1980]. Furthermore, organic-walled dinoflagellate cysts and biochemical classes comprising bulk phytoplanktonic organic carbon are not degraded with identical efficiency in the sedimentary process [Wakeham *et al.*, 1997; Zonneveld *et*

al., 1997]. This being the case, and since different biochemical classes are labeled with different $\delta^{13}C$ signatures [Degens, 1969], the isotopic offset between the alkenones and highly degraded phytoplanktonic detritus should not necessarily be the same as that observed in the living alkenone-producer. In fact, judging from existing literature on this topic [e.g., Hatcher *et al.*, 1983; Benner *et al.*, 1987], one could surmise that the offset would be less than 4.2‰ .

[29] To explore this prospect, Figure 4 was constructed. This scatterplot shows that the ranges of $\delta^{13}C$ for K37:2 and TOC in the unoxidized turbidites (filled circles) are of the same magnitude ($\sim 1\text{‰}$) and these properties correlate positively ($r = +0.71$). Assuming that marine organic carbon contained in the unoxidized turbidite is ^{13}C -enriched by $+4.2\text{‰}$ relative to the phytoplankton biomarker K37:2, a prediction for pure marine organic carbon contained in these deposits has been drawn on the figure (see solid line). Notably, the general trend for actual data from the unoxidized turbidites (filled circles) parallels the predicted line for pure marine organic carbon with an offset of about -1.5‰ . This observation could be construed as evidence that TOC in the unoxidized deposit is predominantly marine-derived and the negative offset merely reflects selective preservation of specific biochemical constituents of marine organic matter, as just described. However, there is considerable scatter in this set of data that warrants an explanation. Almost certainly, scatter reflects to some extent analytical uncertainty. However, it is also conceivable that different quantities in each of these deposits of an independent,

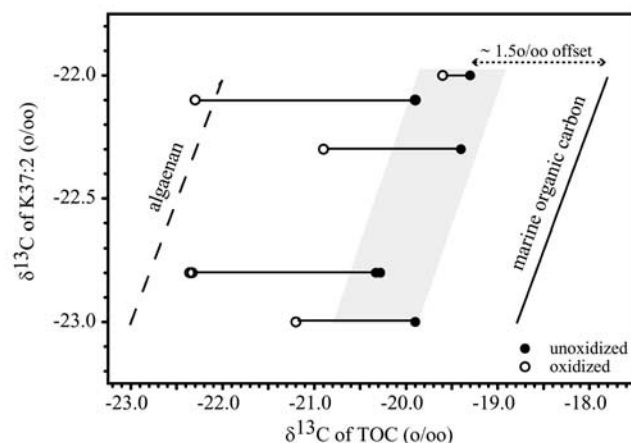


Figure 4. Scatterplot showing the relationship between the stable carbon isotopic composition of the dominant alkenone, K37:2, and TOC in unoxidized (filled circles) and oxidized (open circles) intervals of the various turbidites analyzed in this study (isotopic offsets for TOC indicated by solid connecting lines). Predicted lines for the isotopic composition of pure marine organic carbon (solid) and algaenan (dashed) are also drawn. The shaded area in the graph illustrates the positive correlation noted between these properties ($r = +0.71$) and an apparent, systematic offset of $\sim 1.5\text{‰}$ between data for the unoxidized turbidites and the predicted line for pure marine organic carbon. See text for further details.

^{13}C -depleted source, such as terrestrial organic carbon, accounts for a significant portion of the scatter and at least some fraction of the observed -1.5% offset from the predicted line for pure marine organic carbon.

[30] Further processing of the data set provides insight to an appropriate interpretation. Various studies now show that some, but clearly not all, phytoplankton biosynthesize a polymethylenic polymer as a minor constituent of their living biomass [Gelin *et al.*, 1999]. There is also evidence that this polymer known as “algaenan” is selectively concentrated as phytoplanktonic organic matter degrades in the sedimentary process [de Leeuw and Largeau, 1993, and references therein]. For this reason, a dotted line for pure algaenan has been drawn in Figure 4. The dotted line was predicted assuming that algaenan is biosynthesized by an n-alkyl lipid pathway [de Leeuw and Largeau, 1993] and has an isotopic composition matched by simple marine phytoplanktonic lipids such as K37:2. We then also plotted $\delta^{13}\text{C}$ data for TOC in the oxidized intervals (open circles) assuming that the isotopic composition of K37:2 in these intervals was identical to that in the corresponding unoxidized intervals. This assumption seems geochemically acceptable [Hayes *et al.*, 1990] and was necessary as the isotopic composition of K37:2 in the oxidized intervals has not been formally measured. These modifications to the figure show the isotopic composition of residual TOC from the “burn-down” phenomenon does tend toward the predicted line for pure algaenan, a feature expected if aerobic degradation leads to selective preservation of this biopolymer. However, the degree to which values approximate the algaenan line differs quite significantly from deposit to deposit. This observation seems curious and potentially insightful mechanistically given that (1) the $\delta^{13}\text{C}$ of K37:2 and TOC in the unoxidized intervals of these deposits display such a tight relationship and (2) the percentage loss of TOC by the “burn-down” phenomenon is so consistent in the case of each deposit ($84 \pm 3\%$) but yet bears no significant correlation ($r = -0.085$) with the “burn-down” induced shift in the isotopic composition for TOC. The presence of different, minor but nonetheless significant levels of terrestrial organic carbon in each deposit that is less reactive and somewhat more ^{13}C -depleted than marine organic carbon could explain this otherwise seemingly enigmatic observation.

[31] Hoefs *et al.* [1998a] showed that homologous series of n-alkanes and n-alkenes are major products resulting from pyrolysis of organic matter in unoxidized intervals of other Pliocene and Miocene age turbidites collected during ODP 157. More importantly, they demonstrated that such series become even more predominant when organic matter in oxidized intervals of corresponding turbidites is pyrolyzed. Given algaenan yields such pyrolysis products characteristically and is expected to be ^{13}C -depleted relative to the primary photosynthate of living phytoplankton, they concluded that the -0.3 to -2.9% shift in the $\delta^{13}\text{C}$ of TOC in these deposits upon “burn-down” results from selective preservation of a marine rather than a terrestrial component of organic carbon.

[32] Notably, many higher plants biosynthesize a polymer known as “cutan” which, like algaenan, is also diageneti-

cally resistant [de Leeuw and Largeau, 1993]. Furthermore, both cutan and algaenan when subjected to pyrolysis yield very similar homologous series of n-alkanes and n-alkenes [de Leeuw and Largeau, 1993, and references therein]. Given these facts in light of new perspective provided by the data presentation in Figure 4, we submit that selective preservation of a terrestrial component such as cutan: (1) can account for the observations reported here and by Hoefs *et al.* [1998a] and (2) would explain why the isotopic shift for TOC caused by the “burn-down” phenomenon varies so significantly from deposit to deposit.

4.3. Terrestrial Organic Carbon

[33] In the binary mixing model's original formulation [Prah *et al.*, 1997], choice of any $\delta^{13}\text{C}_{\text{terr}}$ more negative than $\delta^{13}\text{C}_{\text{mar}}$ would yield upon “burn-down” a negative shift in the isotopic composition of residual TOC if the marine component degrades more readily than the terrestrial component. The absolute magnitude of the isotopic shift depends on a combination of three key factors: (1) the fraction of terrestrial organic carbon in the unoxidized turbidite; (2) the magnitude of difference between $\delta^{13}\text{C}_{\text{terr}}$ and $\delta^{13}\text{C}_{\text{mar}}$; and (3) the difference in the relative reactivity of the terrestrial and marine components to the “burn-down” phenomenon.

[34] The $\delta^{13}\text{C}$ composition of individual plant wax n-alkanes has now been determined in unoxidized portions of the Pleistocene age f-turbidite cored at two different geographic locations. Our goal in this effort was to use biomarker isotopic composition to constrain objectively [Jasper and Hayes, 1993] the value of $\delta^{13}\text{C}_{\text{terr}}$ in MAP turbidites. Results show the $\delta^{13}\text{C}$ of plant wax n-alkanes represented by $\text{nC}_{25, 27, 29, 31}$ averages $-25.1 \pm 1.2\%$ (Table 2), a value much more ^{13}C -enriched than expected for pure C3 vegetation ($\sim -34\%$) [Collister *et al.*, 1994]. Two facts suggest significant contribution of organic carbon from C4 vegetation is a likely explanation for the observed ^{13}C -enrichment in these terrestrial biomarkers. First, the source region for organic-rich MAP turbidites, located on the continental slope off NW Africa [de Lange *et al.*, 1987], lays beneath the major route of atmospheric dust transport from Africa into the North Atlantic [Pye, 1987]. Dust samples collected in this wind trajectory contain plant wax n-alkane series that closely match not only the gas chromatographic fingerprint [Prah *et al.*, 1997] but also approximate the compound specific isotopic composition of these molecules preserved in modern sediments from the Atlantic Ocean off NW Africa [Huang *et al.*, 2000] and Pleistocene age sediments from the f-turbidite on MAP (Table 2). Second, the dominant contributor of pollen found in the unoxidized f-turbidite is ascribed to savannah grasses [Keil *et al.*, 1994], plants that in many cases fix carbon via a C4 photosynthetic pathway [see Huang *et al.*, 2000, and references therein].

[35] Given the plant wax n-alkane signature in the f-turbidite reflects both C3 ($\sim -34\%$) and C4 ($\sim -19\%$) contribution [Collister *et al.*, 1994], a simple isotopic mass balance calculation allows the proportion of these inputs to be determined [Huang *et al.*, 2000]. The measured $\delta^{13}\text{C}$ for these compounds ($\sim -25.1\%$) corresponds approximately

to a 40:60 admixture of C3 and C4 inputs, respectively. This interpretive approach can be extended one further step. *Collister et al.* [1994] analyzed $\delta^{13}\text{C}$ in plant wax n-alkanes and TOC from a large collection of fresh C3 and C4 vascular plant tissues and found these biomarkers were on average 4 to 8‰ ^{13}C -depleted relative to TOC with the offset typically greater for C4 than for C3 vegetation. If an isotopic offset of this magnitude existed between plant wax n-alkanes and the terrestrial component of TOC in MAP turbidites, an appropriate $\delta^{13}\text{C}_{\text{terr}}$ value would lay in the range of -17 to -21 ‰, i.e., considerably more positive than the -26 ‰ value originally assigned in the model.

4.4. Chemical Composition of Eolian Dust

[36] In the present study, we also measured the $\delta^{13}\text{C}$ of TOC in one available eolian dust sample collected near the Canary Islands off NW Africa and found that it was surprisingly heavy (-16.7 ‰, Table 2). This value is only slightly more positive than the value of -18.8 ‰ predicted from the $\delta^{13}\text{C}$ of plant wax n-alkanes in the same dust sample (-26.8 ± 1.2 ‰, Table 2) when adjusted using the maximum 8‰ offset described above. On this basis, one could justify assigning such an isotopically enriched value to $\delta^{13}\text{C}_{\text{terr}}$ in the MAP turbidites. This assignment would be problematic for our binary mixing model, however. If $\delta^{13}\text{C}_{\text{terr}}$ is a constant (original model assumption) and isotopically more enriched than $\delta^{13}\text{C}_{\text{mar}}$ (-18.6 ‰, defined in earlier discussion), then it would be impossible for selective preservation of terrestrial organic carbon to cause a negative isotopic shift in TOC. The only way this mechanism could account for such an isotopic shift would be if the terrestrial input were comprised of at least two components with distinctly different isotopic compositions and sensitivity to oxidative degradation. Judging from observations (Figure 4), the more refractory, selectively preserved terrestrial component(s) would need to be labeled with a $\delta^{13}\text{C}$ at least as negative as -23 ‰.

[37] Given the yet limited geochemical information now available, we cannot formally test the latter possibility. However, examination of other data obtained from analysis of the dust sample lends support to the latter possibility. The molar ratio for $\text{C}/\text{N}_{\text{tot}}$ in the dust sample was 10.0, a value comparable to that measured in each unoxidized turbidite (10.5 to 13.2, Table 1). If dust with this $\text{C}/\text{N}_{\text{tot}}$ composition ultimately represents a significant vector for terrestrial input to these sediments and this input contributes significantly to the TOC and N_{tot} in the oxidized turbidites, its organic carbon content could not be impervious to the “burn-down” phenomenon. As a consequence of oxidation, $\text{C}/\text{N}_{\text{tot}}$ in the turbidite is decreased to values as low as 4–5 (Table 1). Unless retention within clays of ammonium ion [Muller, 1977] generated by remineralization of marine organic matter accounts for this decline [Cowie et al., 1998], compositional requirements would necessitate the organic carbon content of the dust is lost up to 50% more efficiently than the nitrogen content of the dust. Assuming that (1) organic carbon in the dust experiences such preferential loss, (2) its composition initially reflects an equal contribution from C3 and C4 sources and (3) these components do

not degrade with identical efficiencies, a nonconstant value of $\delta^{13}\text{C}_{\text{terr}}$ would be required to isotopically track the quantitative behavior of this terrestrial component as the turbidite is altered progressively by the “burn-down” phenomenon. This argument can be extended one important step farther. If the ^{13}C -enriched C4 component was more susceptible to oxidative loss than the ^{13}C -depleted C3 component, then the $\delta^{13}\text{C}_{\text{terr}}$ value used to quantify residual terrestrial organic carbon in the oxidized deposit would need to be adjusted more negative as the oxidation process progressed.

[38] The potential quantitative importance of terrestrial input in setting the composition of the oxidized turbidite is further highlighted by the result from analysis of the total nitrogen isotopic composition in the eolian dust sample. N_{tot} in the dust was found to be unexpectedly ^{15}N -enriched (i.e., $+10.9$ ‰, Table 2). This finding is notable given the “burn-down” phenomenon yields a positive isotopic shift in the N_{tot} of all turbidites (Table 1). By conventional thinking [Cowie et al., 1998], such a nitrogen isotopic shift cannot be explained by selective preservation of average terrestrial organic matter. A negative shift in $\delta^{15}\text{N}$ would more likely accompany such a process.

[39] Based on results from analysis of yet a single eolian dust sample, we submit that some as yet unquantified portion of the ^{15}N -enriched signal for N_{tot} in the oxidized intervals reflects an eolian input from the land which, like terrestrial organic carbon, is selectively preserved during the “burn-down” phenomenon. The allochthonous, ^{15}N -enriched material remains undescribed but could take the chemical form of organic or inorganic nitrogen residues in dust originating from terrestrial environments where intense N-cycling processes (e.g., denitrification; ammonification) have led at some prior time to loss by volatilization of ^{15}N -depleted gases such as N_2 , N_2O and NH_3 .

4.5. Diagenetic Impact on the Alkenone Temperature Index

[40] The percentage loss of LCK and other lipid biomarkers of phytoplankton origin (Tables 1 and 3) consistently exceed that documented for TOC in all turbidites examined (Figure 1). However, despite loss as extreme as 99%, the original U_{37}^{K} signature is relatively unchanged by the “burn-down” phenomenon. Such results [Prahl et al., 1989; Hoefs et al., 1998b] (Table 1) are now cited as clear evidence that U_{37}^{K} is insensitive to significant change in the sedimentary process and, at least in this regard, provides a parameter well-suited for use in paleothermometry [Grimalt et al., 2000].

[41] We constructed a graph (Figure 5) illustrating how selective degradation of alkenones would quantitatively bias a paleotemperature estimate as a function of any U_{37}^{K} [Hoefs et al., 1998b]. Positive and negative ΔT values depict the consequence of selective K37:3 and K37:2 degradation, respectively. Data from prior study of the f-turbidite [Prahl et al., 1989] and our present study of four older turbidites from ODP 157 are also plotted on the graph. Error bars associated with the filled circles depict the uncertainty ($\pm 1\sigma$) in the paleotemperature estimate based on U_{37}^{K} measured in the unoxidized turbidite. Open circles depict the bias in the

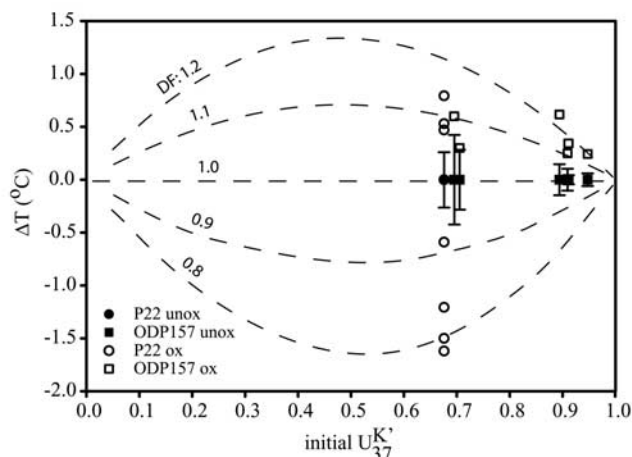


Figure 5. Predicted offset in paleotemperature caused by the perceived selective degradation of the triunsaturated (+ ΔT) and diunsaturated ($-\Delta T$) C_{37} alkenone during aerobic “burn-down” of the various turbidites analyzed (open symbols). Error bars associated with solid symbols indicate uncertainty in the paleotemperature estimate based on replicate $U_{37}^{K'}$ measurements in different unoxidized intervals of the same turbidite. Dashed curves show how the magnitude of ΔT would vary for any initial $U_{37}^{K'}$ given 10% and 20% selectivity for alkenone degradation during “burn-down.” Predicted behavior was determined using the concept of a relative degradation factor (DF) in a modeling approach described more specifically by Hoefs *et al.* [1998b]. ΔT estimates are calculated from the difference between the $U_{37}^{K'}$ measurement in the oxidized relative to the unoxidized turbidite interval assuming a change of 0.034 $U_{37}^{K'}$ units per $^{\circ}C$ [Prahl *et al.*, 1988].

paleotemperature estimate based on analysis of $U_{37}^{K'}$ in corresponding oxidized intervals. These data are consistent with those of Hoefs *et al.* [1998b], which indicated a positive temperature bias, evidence for selective $K_{37}:3$ degradation. Our data contrast theirs in key respects, however. The relative degradation factor (DF) required to describe our data is much less than 1.5. More importantly, the DF for the f-turbidite, marked by a $U_{37}^{K'}$ value closer to the mid-range for this index, is lower than that calculated for the other turbidites marked by $U_{37}^{K'}$ values near the upper limit for this property.

[42] Data for the more extensive set of oxidized samples collected stratigraphically above the oxidation front identified in core 90P22 are also plotted in Figure 5 (see open and filled squares). These data are again accountable using a DF much lower than 1.5. In fact, some are described by DF values less than 1, suggesting at face value that the diunsaturated C_{37} ketone was more sensitive to degradation than the triunsaturated. This explanation seems geochemically unsatisfactory, however. Given the range of $U_{37}^{K'}$ values we now document in unoxidized portions of the f-turbidite sampled with depth in a given core (0.669–0.686, Table 3) and spatially in different cores (0.669–0.712, Tables 1 and 3), it seems more likely that apparent DF values less than unity reflect minor chemical inhomogeneity in the massive distal turbidite deposit and not an authentic diagenetic consequence of the “burn-down” phenomenon.

geinity in the massive distal turbidite deposit and not an authentic diagenetic consequence of the “burn-down” phenomenon.

5. Conclusions

[43] There is no doubt that terrestrial organic carbon is present at some level in the organic-rich MAP turbidites. Furthermore, the isotopic composition of bulk terrestrial organic carbon introduced to the source region for these turbidites and contained in the unoxidized intervals may be quite ^{13}C -enriched owing to a significant contribution from C_4 plants [Huang *et al.*, 2000]. As such, reliable quantification of the terrestrial contribution would be impossible from measurement of $\delta^{13}C$ in TOC alone given that the terrestrial material is not just selectively preserved relative to marine material but perhaps even selectively preserved on an isotopic basis.

[44] Certainly, there are more fine details to work out before the consequences of “burn-down” and even less severe oxidation phenomena on the organic carbon composition preserved in open-ocean sediments are fully understood. What has now been learned organically from study of MAP “burn-down” turbidites, however, highlights an important conclusion. Owing to selective preservation phenomena, a research goal such as pCO_2 reconstruction using the $\delta^{13}C$ record of TOC in sediments [e.g., Goericke and Fry, 1994] is fraught with uncertainty, whether the marine record is “contaminated” with terrestrial material or not. If such a goal is at all achievable [e.g., Laws *et al.*, 1995; Bidigare *et al.*, 1997, 1999], isotopic analysis of a specific molecular component of marine organic carbon such as the alkenones would seem the only tractable analytical approach [Laws *et al.*, 2002] to circumvent the problems identified in the present study.

[45] Our examination of MAP turbidites reinforces the view that greatest loss of alkenones occurs in the sedimentary process under aerobic diagenetic conditions [Prahl *et al.*, 2001; Wakeham *et al.*, 2002]. It also demonstrates that aerobic degradation of alkenones occurs with at most 20% selectivity for the triunsaturated over the diunsaturated C_{37} compound. Given an initial $U_{37}^{K'}$ of 0.4, such selectivity would lead to a bias in paleotemperature estimates no greater than $+1.3^{\circ}C$. In fact, this magnitude of over-estimate is considered an absolute maximum since the impact of selective compound degradation on $U_{37}^{K'}$ is nonlinear and greatest when the unsaturation index has a value of ~ 0.4 [Hoefs *et al.*, 1998b]. Our findings fully endorse the viewpoint conveyed recently by the research community [Grimalt *et al.*, 2000] that the paleotemperature index $U_{37}^{K'}$, once set biosynthetically by alkenone producers, is not extremely sensitive to diagenetic change in the sedimentary process.

[46] **Acknowledgments.** We are grateful to Brian Popp (University of Hawaii, Manoa) for use of his irmGCMS facility, to R. Keil and M. Pagani for thoughtful reviews of the initial manuscript submitted for publication, to NSF for financial support of this organic geochemical research through grant OCE-961685 (FGP) and ultimately to the RDG, NWO and ODP for making it possible to study geochemical processes on MAP.

References

- Benner, R., M. L. Fogel, E. K. Sprague, and R. E. Hodson, Depletion of ^{13}C in lignin and its implications for stable carbon isotope studies, *Nature*, 329, 708–710, 1987.
- Bidigare, R. R., et al., Consistent fractionation of ^{13}C in nature and in the laboratory: Growth-rate effects in some Haptophyte algae, *Global Biogeochem. Cycles*, 11, 279–292, 1997.
- Bidigare, R. R., et al., Iron-stimulated changes in ^{13}C fractionation and export by equatorial Pacific phytoplankton: Toward a paleogrowth rate proxy, *Paleoceanography*, 14, 589–595, 1999.
- Brassell, S. C., Applications of biomarkers for delineating marine paleoclimatic fluctuations during the Pleistocene, in *Organic Geochemistry: Principles and Applications*, edited by M. H. Engel and S. A. Macko, pp. 699–738, Plenum, New York, 1993.
- Buckley, D. E., and R. E. Cranston, Early diagenesis in deep-sea turbidites: The imprint of paleo-oxidation zones, *Geochim. Cosmochim. Acta*, 52, 2925–2939, 1988.
- Christie, W. W., *Lipid Analysis: Isolation, Separation, Identification and Structural Analysis of Lipids*, 338 pp., Pergamon, New York, 1973.
- Collister, M. W., G. Rieley, B. Stern, G. Eglinton, and B. Fry, Compound-specific $\delta^{13}\text{C}$ analyses of leaf lipids from plants with differing carbon dioxide metabolisms, *Organic Geochem.*, 21, 619–627, 1994.
- Cowie, G. L., J. I. Hedges, F. G. Prahl, and G. J. De Lange, Elemental and major biochemical changes across an oxidation front in a relict turbidite: An oxygen effect, *Geochim. Cosmochim. Acta*, 59, 33–46, 1995.
- Cowie, G., S. Calvert, G. De Lange, R. Keil, and J. Hedges, Extents and implications of organic matter alteration at oxidation fronts in turbidites from the Madeira Abyssal Plain, *Ocean Drill. Project Sci. Results*, 157, 581–589, 1998.
- Degens, E. T., Biogeochemistry of stable carbon isotopes, in *Organic Geochemistry*, edited by G. Eglinton and E. J. T. Murphy, pp. 304–329, Springer-Verlag, New York, 1969.
- de Lange, G. J., Distribution of exchangeable, fixed, organic and total nitrogen in interbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic, *Mar. Geol.*, 109, 95–114, 1992.
- de Lange, G. J., Oxid versus anoxic diagenetic alteration of turbiditic sediments in the Madeira Abyssal Plain, eastern North Atlantic, *Ocean Drill. Project Sci. Results*, 157, 573–579, 1995.
- de Lange, G. J., Oxid vs. anoxic diagenetic alteration of turbiditic sediments in the Madeira Abyssal Plain, Eastern North Atlantic, *Ocean Drill. Project Sci. Results*, 157, 573–580, 1998.
- de Lange, G. J., O. Jarvis, and A. Kuijpers, Geochemical characteristics and provenance of late Quaternary sediments from the Madeira Abyssal Plain, North Atlantic, in *Geology and Geochemistry of Abyssal Plains*, *Geol. Soc. Spec. Publ.*, vol. 31, edited by P. P. E. Weaver and J. Thomson, pp. 147–165, Geol. Soc., London, 1987.
- de Lange, G. J., B. van Os, P. A. Pruyssers, J. J. Middelburg, D. Castradori, P. van Santvoort, P. Muller, J. Eggenkamp, and F. G. Prahl, Possible early diagenetic alteration of paleoproxies, in *Carbon Cycling in the Glacial Ocean: Constraints on Ocean's Role in Global Climate Change*, *NATO Ser.*, vol. 17, edited by R. Zahn, pp. 225–258, Springer-Verlag, New York, 1994.
- de Leeuw, J. W., and C. Largeau, A review of macromolecular organic compounds that comprise living organisms and their role in kerogen, coal, and petroleum formation, in *Organic Geochemistry: Principles and Applications*, edited by M. H. Engel and S. A. Macko, pp. 23–72, Plenum, New York, 1993.
- de Leeuw, J. W., W. I. C. Rijpstra, and P. A. Schenck, The occurrence and identification of C_{30} , C_{31} and C_{32} alkan-1,15-diols and alkan-15-one-1-ols in Unit I and Unit II Black Sea sediments, *Geochim. Cosmochim. Acta*, 45, 2281–2285, 1981.
- Gelin, F., J. K. Volkman, C. Largeau, S. Derenne, J. S. Sinninghe Damste, and J. W. de Leeuw, Distribution of aliphatic, nonhydrolyzable biopolymers in marine microalgae, *Organic Geochem.*, 30, 147–159, 1999.
- Goericke, R., and B. Fry, Variations of marine phytoplankton $\delta^{13}\text{C}$ with latitude, temperature, and dissolved CO_2 in the world ocean, *Global Biogeochem. Cycles*, 8, 85–90, 1994.
- Goossens, J., W. I. C. Rijpstra, R. R. Duren, J. W. de Leeuw, and P. A. Schenck, Bacterial contribution to sedimentary organic matter: a comparative study of lipid moieties in bacteria and recent sediments, *Organic Geochem.*, 10, 683–696, 1986.
- Grimalt, J. O., J. Rullkotter, M.-A. Sicre, R. Summons, J. Farrington, H. R. Harvey, M. Goni, and K. Sawada, Modifications of the C_{37} alkenone and alkenoate composition in the water column and sediment: Possible implications for sea surface temperature estimates in paleoceanography, *Geochim. Geophys. Geosyst.*, 1, paper number 2000GC000053, 2000.
- Hartnett, H. E., R. G. Keil, J. I. Hedges, and A. H. Devol, Influence of oxygen exposure time on organic carbon preservation in continental margin sediments, *Nature*, 391, 572–574, 1998.
- Hatcher, P. G., E. C. Spiker, N. M. Szeverenyi, and G. E. Maciel, Selective preservation and origin of petroleum-forming aquatic kerogen, *Nature*, 305, 498–501, 1983.
- Hayes, J. M., K. H. Freeman, B. N. Popp, and C. H. Hoham, Compound-specific isotopic analyses: A novel tool for reconstruction of ancient biogeochemical processes, *Organic Geochem.*, 16, 1115–1128, 1990.
- Hedges, J. I., F. S. Hu, A. H. Devol, H. E. Hartnett, E. Tsamakis, and R. G. Keil, Sedimentary organic matter preservation: A test for selective degradation under oxic conditions, *Am. J. Sci.*, 299, 529–555, 1999.
- Hoefs, M. J. L., J. S. Sinninghe Damste, G. J. de Lange, and G. W. de Leeuw, Changes in kerogen composition across an oxidation front in Madeira Abyssal Plain turbidites as revealed by pyrolysis GC-MS, *Proc. Ocean Drill. Prog., Sci. Results*, 157, 591–607, 1998a.
- Hoefs, M. J. L., G. J. M. Versteegh, W. I. C. Rijpstra, J. W. de Leeuw, and J. S. Sinninghe Damste, Postdepositional oxic degradation of alkenones: Implications for the measurement of palaeo-sea surface temperatures, *Paleoceanography*, 13, 42–49, 1998b.
- Hoefs, M. J. L., W. I. C. Rijpstra, and J. S. Sinninghe Damste, The influence of oxic degradation on the sedimentary biomarker record, I: Evidence from Madeira Abyssal Plain turbidites, *Geochim. Cosmochim. Acta*, 66, 2719–2735, 2002.
- Huang, Y., L. Dupont, M. Sarnthein, J. M. Hayes, and G. Eglinton, Mapping of C_4 plant input from northwest Africa into northeast Atlantic sediments, *Geochim. Cosmochim. Acta*, 64, 3505–3513, 2000.
- Jasper, J. P., and J. M. Hayes, Refined estimation of marine and terrigenous contributions to sedimentary carbon, *Global Biogeochem. Cycles*, 7, 451–461, 1993.
- Keil, R. G., F. S. Hu, E. C. Tsamakis, and J. I. Hedges, Pollen in marine sediments as an indicator of oxidation of organic matter, *Nature*, 369, 639–641, 1994.
- Kolattukudy, P. E., (Ed.), *Chemistry and Biochemistry of Natural Waxes*, 459 pp., Elsevier Sci., New York, 1976.
- Laws, E. A., B. N. Popp, R. P. Bidigare, M. C. Kennicutt, and S. A. Macko, Dependence of phytoplankton carbon isotopic composition on growth rate and $[\text{CO}_2]_{\text{aq}}$: Theoretical considerations and experimental results, *Geochim. Cosmochim. Acta*, 59, 1131–1138, 1995.
- Laws, E. A., B. N. Popp, N. Cassar, and J. Tanimoto, ^{13}C discrimination patterns in oceanic phytoplankton: Likely influence of CO_2 concentrating mechanisms, and implications for paleoreconstruction, *Funct. Plant Biol.*, 29, 323–333, 2002.
- Muller, P. J., C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays, *Geochim. Cosmochim. Acta*, 41, 765–776, 1977.
- Popp, B. N., F. Kenig, S. G. Wakeham, E. A. Laws, and R. R. Bidigare, Does growth rate affect ketone unsaturation and intracellular carbon isotopic variability in *Emiliania huxleyi*?, *Paleoceanography*, 13, 35–41, 1998.
- Prahl, F. G., L. A. Muehlhausen, and D. L. Zahnle, Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions, *Geochim. Cosmochim. Acta*, 52, 2303–2310, 1988.
- Prahl, F. G., G. J. de Lange, M. Lyle, and M. A. Sparrow, Postdepositional stability of long-chain alkenones under contrasting redox conditions, *Nature*, 341, 434–437, 1989.
- Prahl, F. G., J. M. Hayes, and T.-M. Xie, Diplopene: An indicator of terrigenous organic carbon in Washington coastal sediments, *Limnol. Oceanogr.*, 37, 1290–1300, 1992.
- Prahl, F. G., G. J. de Lange, S. Scholten, and G. L. Cowie, A case of postdepositional aerobic degradation of terrestrial organic matter in turbidite deposits from the Madeira Abyssal Plain, *Organic Geochem.*, 27, 141–152, 1997.
- Prahl, F. G., C. H. Pilskaln, and M. A. Sparrow, Seasonal record for alkenones in sedimentary particles from the Gulf of Maine, *Deep Sea Res.*, 48, 515–528, 2001.
- Pye, K., (Ed.), *Aeolian Dust and Dust Deposits*, 334 pp., Academic, San Diego, Calif., 1987.
- Suess, E., Particulate organic carbon flux in the oceans—Surface productivity and oxygen utilization, *Nature*, 288, 260–263, 1980.
- Thomson, J., S. Colley, N. C. Higgs, D. Hydes, T. R. S. Wilson, and J. Sorensen, Geochemical oxidation fronts in NE Atlantic distal turbidites and their effects on the sedimentary record, in *Geology and Geochemistry of Abyssal Plains*,

- Geol. Soc. Spec. Publ.*, vol. 31, edited by P. P. E. Weaver and J. Thomson, pp. 167–177, Geol. Soc., London, 1987.
- Versteegh, G. J. M., H.-J. Bosch, and J. W. De Leeuw, Potential palaeoenvironmental information of C₂₄ to C₃₆ mid-chain diols, ketols and mid-chain hydroxy fatty acids: A critical review, *Organic Geochem.*, 27, 1–13, 1997.
- Wakeham, S. G., C. Lee, J. I. Hedges, P. J. Hernes, and M. L. Peterson, Molecular indicators of diagenetic status in marine organic matter, *Geochim. Cosmochim. Acta*, 61, 5363–5369, 1997.
- Wakeham, S. G., M. L. Peterson, J. I. Hedges, and C. Lee, Lipid biomarker fluxes in the Arabian Sea, with comparison to the equatorial Pacific Ocean, *Deep Sea Res., Part II*, 49, 2265–2301, 2002.
- Weaver, P. P. E., H.-U. Schmincke, J. V. Firth, and W. Duffield (Eds.), *Proceedings of the Ocean Drilling Program, Scientific Results*, vol. 157, Ocean Drill. Prog., College Station, Tex., 1998. (Available at http://www-odp.tamu.edu/publications/157_SR/157TOC.HTM.)
- Wilson, T. R. S., J. Thomson, S. Colley, D. J. Hydes, N. C. Higgs, and J. Sorensen, Early organic diagenesis: The significance of progressive subsurface oxidation fronts in pelagic sediments, *Geochim. Cosmochim. Acta*, 49, 811–822, 1985.
- Zonneveld, K. A. F., G. J. M. Versteegh, and G. J. de Lange, Preservation of organic-walled dinoflagellate cysts in different oxygen regimes: A 10,000 year natural experiment, *Mar. Micropaleontol.*, 29, 393–405, 1997.
-
- G. L. Cowie, Marine Geosciences Unit, Geology and Geophysics Department, University of Edinburgh, West Mains Road, Edinburgh EH9 3JW, UK. (Greg.Cowie@glg.ed.ac.uk)
- G. J. de Lange, Institute of Earth Sciences, Department of Geochemistry, Utrecht University, 3584 CD, Utrecht, Netherlands. (gdelange@geo.uu.nl)
- F. G. Prahl and M. A. Sparrow, College of Oceanic and Atmospheric Sciences, Oregon State University, Corvallis, OR 97331-5503, USA. (fpahl@coas.oregonstate.edu)